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Particle size of ground bacterial cellulose affecting mechanical, thermal, and moisture barrier properties of PLA/BC biocomposites

Meechai Luddee[a], Sommai Pivsa-Art[d], Sarote Sirisansaneeyakul[b,c], Chiravoot Pechyen[a,c,*]

[a]*Department of Packaging and Materials Technology, Kasetsart University, Chatuchak, Bangkok, 10900, Thailand*
[b]*Department of Biotechnology, Kasetsart University, Chatuchak, Bangkok, 10900, Thailand*
[c]*Center for Advanced Studies in Tropical Natural Resources, National Research University-Kasetsart University, Bangkok, 10900, Thailand*
[d]*Department of Materials and Metallurgical Engineering, Rajamangala University of Technology Thanyaburi, Pathum Thani 12110, Thailand*

Abstract

The effect of the particle sizes of bacterial cellulose (BC) that used as reinforcement for polylactic acid (PLA) biocomposites was investigated. The content of BC in PLA was fixed at 5 phr and various BC particle sizes were investigated, i.e., <90, 106-125, 150-180, 180-250, and 250-300 μm, respectively. The results showed that tensile strength and elongation of PLA/BC biocomposites decreased with increasing the BC particle sizes from <90 to 150-180 μm. However, the particle sizes larger than 180 μm were resulted in decreased tensile strength and elongation of PLA/BC biocomposites.Whereas, the modulus decreased with an increase of all particle sizes of BC tested. From the scanning electron microscopy (SEM) the microstructures showed that loading the smaller BC particle sizes in biocomposites in PLA matrix gave the smoother biocomposites than those from the larger BC particle sizes. This implied that the smaller BC size can disperse in PLA matrix better than the larger particle size. For the thermal properties, BC had influenced on the peak crystallisation temperature of biocomposite in which the temperature of neat PLA film decreased from 119.8 to 112.2-113 °C of the derived composite films. This behaviour indicated that BC can induce crystal nucleation of the PLA polymer. However, BC did not affect on the glass transition temperature (T_g) and melting temperature (T_m). The water vapor permeability increased with an increase of the particle sizes of ground BC.

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Keywords: Bacterial cellulose; Biocomposite; Particle size; PLA

* Corresponding author. Tel.: +662-562-5295; fax: +662-562-5046
E-mail address: chiravoot.p@ku.ac.th

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1. Introduction

Bacterial cellulose (BC) is one of the most abundant biopolymers on earth. It can be synthesized biologically by bacteria. Especially, *Acetobacter xylinum* is mostly often used to produce bacterial cellulose due to its ability to grow under various conditions, e.g. static culture, submerged culture and rotating disc bioreactor [1-2]. BC has more purity as compared to plant celluloses as it does not contain hemicelluloses and/or lignin that need to be removed prior to processing. Furthermore, BC exhibits many unique properties, including higher crystallinity, degree of polymerization, water absorption/retaining capacity, tensile strength, and stronger biological adaptability. BC has been applied in the food industry, bone regeneration [3], tissue engineering [4], and as reinforcement in nanocomposites [5]. There are various processes used to prepare the PLA/BC biocomposites. These are melt-mixing/extrusion [6-7], solution casting [8-9], and master batch preparation with solvent mixing followed by extrusion [10]. These results observed that differences in the cellulose morphology of wood fiber, cellulose fiber, microcrystalline cellulose, and cellulose nanofiber could improve the mechanical and thermal properties. In addition, an incorporation of cellulose nanofiber also improved the oxygen and water vapor barrier properties [9]. However, the biodegradability of biocomposites decreased, as their water absorption was found to be lower than that of neat polymer [11].

The objective of this study is to investigate the effect of BC particle sizes on thermal, mechanical, and water barrier properties of fully green PLA/BC biocomposites prepared from the casting extrusion process.

2. Materials and methods

2.1 Materials

Polylactic acid (PLA, 4043D grade), used as matrix phase was purchased from Nature Works® with a density of 1.24 g/cm^3 and melting point of 145-160 °C. Bacterial cellulose pellicle was obtained from Ampol food processing Co, Ltd. Thailand.

2.2 Preparation of bacterial cellulose powder

Bacterial cellulose pellicle was washed with tap water to remove the residual culture medium, boiled in 1 wt.% aqueous NaOH for 30 min to remove bacterial cells, and boiled in tap water until the pH was neutral (pH 5-7). Thereafter, the clean bacterial cellulose pellicle was pressed in a hydraulic pressing machine, and dried up in the hot air oven at 60 °C for 24 hours. The resultant bacterial cellulose sheets were then ground with a rotor milling machine to produce a cellulose powder. Finally, the different BC particle sizes were prepared by sieving method.

2.3 Preparation of PLA/BC biocomposite films

The PLA/BC biocomposite films were prepared by using film casting extrusion process. Initially, PLA pellet and BC powder were dried at 80 °C for 12 hours in a hot air oven. Then, both PLA and BC were manually mixed, and the PLA/BC mixture was subsequently fed into the extruder for melt compounding with a screw speed of 60 rpm, the temperature profiles were 50 (feeding zone), 150, 160, 170, 180 °C (die zone), and this was kept at a melt temperature of 180 °C. The extrudate was cooled in a water bath and subsequently granulated by a pelletizer. Thus, the biocomposite films were prepared by film casting machine. The obtained biocomposite pellets were first dried at 60 °C in a hot air oven for 4 hours, after that fed into the film casting machine, varying the temperature from 140 (feed zone) to 170 °C (die zone), and the screw speed was kept constant at 55 rpm. Various formulations of the biocomposites were prepared, as shown in Table 1.

Table 1. Formulation of the PLA/BC biocomposites.

Samples	Designed	BC particle size (μm)	BC (phr)	PLA (wt.%)
1	Neat PLA	PLA	-	100
2	PLA/BC <90 μm	<90	5	100
3	PLA/BC 106-125 μm	106-125	5	100
4	PLA/BC 150-180 μm	150-180	5	100
5	PLA/BC 180-250μm	180-250	5	100

2.4 Characterization

Tensile properties were determined according to ASTM D638 using a universal testing machine (Model 5965, Instron, USA). The samples were tested at room temperature with a gauge length of 50 mm. Cross head speed and load cell were 10 mm/min and 5 kN, respectively.

The differential scanning calorimeter (DSC) (Mettler Toledo DSC822, Switzerland) was applied to determine the thermal properties (glass transition temperature (T_g), melting temperature (T_m) and degree of crystallinity (X_C)) of the samples approximately 5.0 mg. For heating-cooling-heating measurements, the following steps were performed: heat at 10 °C/min from 0 to 200 °C; isotherm at 200 °C for 5 min; cool at 10 °C/min from 200 to 0 °C; heat at 10 °C/min from 0 to 200 °C; isotherm at 200 °C for 5 min; cool at 10 °C/min from 200 to 0 °C. The melting temperature was calculated from the midpoint of the base-line shift of the DSC thermogram. The degree of crystallinity of PLA/BC composites was calculated from the second thermal scan as following:

$$X_C = \frac{(\Delta H_m - \Delta H_C)}{\Delta H_m^0 \times w} \times 100 \quad (1)$$

where X_C is the crystallinity, w is the weight fraction of PLA in the biocomposite, ΔH_m is the melting enthalpy, ΔH_C is the enthalphy of cold crystallization from DSC measurements, and ΔH^0_m is the melting enthalpy for 100% crystalline PLA (93 J/g) [8].

The microstructures of biocomposites were investigated using the scanning electron microscopy (SEM). Surface and freeze fractured surfaces were determined with a Philips, XL30 SEM (Japan). The acceleration voltage was 10 kV and samples were sputter-coated with gold in order to avoid charging.

3. Results and discussion

3.1 Tensile properties

The tensile properties of the PLA/BC biocomposites were illustrated in Fig. 1-3. The results indicated that tensile strength, elongation at break and Young's modulus of PLA/BC biocomposites were all lower than those of the neat PLA. These were disagreed with those reported previously, that incorporating different types of celluloses such as ground bacterial cellulose [6], wood fiber, cellulose fiber and microcrystalline cellulose [7], and cellulose nanofiber [10] into the PLA matrix, resulting in an increase of tensile strength (Fig. 1) and Young's modulus (Fig. 3), but were agreeable to decreased elongation (Fig. 2), as compared to neat PLA. As compared with PLA, BC was more hydrophilic, therefore, the interfacial adhesion between BC and PLA was found to lower. As a result, the BC had poor dispersibility in PLA, and an agglomeration of cellulose by hydrogen bonding occurred [9]. Among the PLA/BC biocomposites, tensile strength and elongation decreased substantially with an increase of the particle sizes of BC, namely <90, 106-125, and 150-180 μm, respectively. However, addition of BC with the particle sizes of 180-250 μm (PLA/BC 180-250 μm) resulted in an increase of tensile strength and elongation. The tensile strength and elongation at break of PLA/BC 180-250 μm was increased might be due to loading the larger particle size of BC

leads to require more tensile strength to pull the fiber out from matrix [14]. Another possible reason is the degree of crystallinity observing at the first thermal scan of PLA/BC 180-250 μm was higher than other PLA/BC biocomposites. A degree of crystallinity at the first thermal scan of PLA/BC <90, PLA/BC 106-125, PLA/BC 150-180, and PLA/BC 180-250 μm were 3.6, 4.2, 2.6, and 5.9 %, respectively. Moreover, the biocomposite incorporated with larger sizes of BC gave the resultant biocomposites with larger crystallite size. As compared with the wood fiber (150-750 μm) and cellulose fiber (20-30 μm) incorporated into the PLA matrix [7], the larger particle size of cellulose caused the crystallite size lager. In addition, the melt peak (T_m) of PLA/BC 180-250 μm was higher than other biocomposites. This is indicative of the crystallite size of PLA/BC 180-250 μm might be larger [15]. The values of Young's modulus of all biocomposites found in this study were lower, as compared to neat PLA. This indicated clearly that the crystallinity of PLA/BC biocomposites was lower than that of the neat PLA alone. This might be BC affect to the crystallization behavior of PLA matrix. In previous work [7], incorporation of the cellulose into PLA matrix, the nucleation and growth occurred both on surface of reinforcement (transcrystallization) and PLA matrix (bulk crystallization). They reported that under cold crystallization PLA incorporated with cellulose, bulk crystallization was predominated and transcrystallization may be suppressed. This leads to the degree of crystallization of biocomposites was lower than neat PLA.

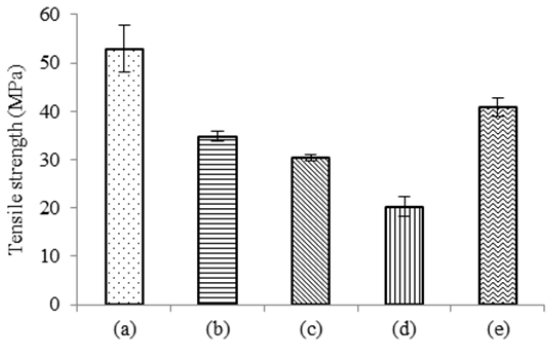

Fig. 1. Effect of BC particle sizes on tensile strength of the biocomposites: (a) neat PLA; (b) PLA/BC <90; (c) PLA/BC 106-125; (d) PLA/BC 150-180; (e) PLA/BC 180-250 μm.

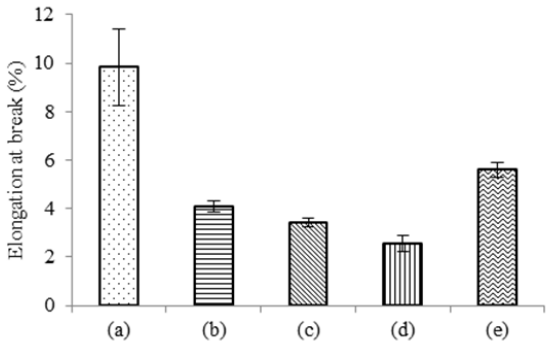

Fig.2. Effect of BC particle sizes on elongation at break of the biocomposites: (a) neat PLA; (b) PLA/BC <90; (c) PLA/BC 106-125; (d) PLA/BC 150-180; (e) PLA/BC 180-250 μm.

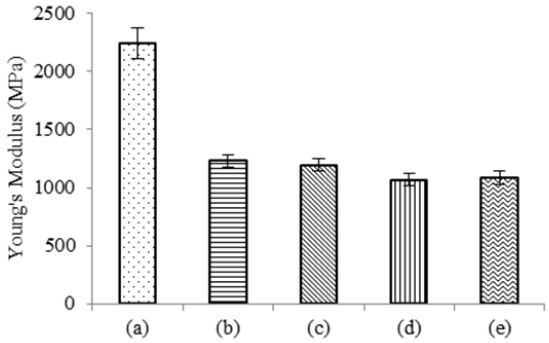

Fig. 3. Effect of BC particle sizes on Young's Modulus of the biocomposites: (a) neat PLA; (b) PLA/BC <90; (c) PLA/BC 106-125; (d) PLA/BC 150-180; (e) PLA/BC 180-250 μm.

3.2 Thermal properties

Table 2. The effect of BC particle sizes on thermal properties of the PLA/BC biocomposites.

Samples	T_g (°C)	T_{cc} (°C)	T_m (°C)	T_d (°C)	ΔH_m (J/g)	ΔH_c (J/g)	X_c (%)
Neat PLA	60.0	119.8	150.4	362.0	14.4	9.9	4.8
PLA/BC <90 μm	59.5	112.2	151.1	360.2	23.3	19.3	4.4
PLA/BC 106-125 μm	59.5	112.2	151.4	360.3	23.2	19.2	4.4
PLA/BC 150-180 μm	59.9	113.0	151.5	360.4	23.3	20.1	3.6
PLA/BC 180-250 μm	59.9	113.0	151.8	360.8	23.3	20.1	3.6

The thermal properties of PLA/BC biocomposites compared to the neat PLA were summarized in Table 2. BC was found to influence on the thermal properties of PLA, especially its crystallization behavior. The peak crystallization temperature decreased to 112.2 -113 °C for the composite, as compared with 119.8 °C of the neat PLA film. This behavior indicated that the bacterial cellulose can induce crystal nucleation of the PLA polymer, which implied that this bacterial cellulose material can probably be used as a nucleating agent for PLA. This is in agreement with the results obtained by similar studies [12]. However, the degree of crystallinity of biocomposites was slightly lower than the neat PLA, because the biocomposite processing did not activate the crystallization completely. Also the enthalphy of cold crystallization (ΔH_C) from second heating of PLA/BC biocomposite is higher than the neat PLA. This indicated that the crystallization of PLA/BC biocomposite indeed was not completed. However, an improvement of biocomposite crystallization can achieve with heat treatment process. Some previous works [4,13] reported that heat treatment improved the crystallization ability of biocomposite. Thus, the heat treatment of biocomposites promisingly promotes the crystallization. Considering amongst PLA/BC biocomposites in the current work, the biocomposite incorporated with BC particle size 250-300 μm gave the highest crystallinity. For the glass transition temperature (T_g) of the PLA/BC biocomposites, the BC particle size did not affect the chain mobility of PLA. It was revealed that the similar values of T_g were obtained (Table 2). Both neat PLA and PLA/BC biocomposites had a peak position of T_g at 55.9-60 °C. The process might not change the degree of crystallinity of biocomposites incorporating BC into the PLA matrix. As a result, the chain mobility of PLA was not affected. The reason for this could explain by the fact that the chain mobility was restricted by increased crystallite region of polymer matrix [7,10]. In addition, BC did not affect to the melting temperature (T_m) of the PLA/BC biocomposites. A peak was observed at 150.4-151.8 °C. This behavior might be the degree of crystallinity and the crystallite size of biocomposites were not much changed to influence the T_m of biocomposites. These are correlated well to the previous report [7], which the T_m tends to increase with increasing the crystallite size of polymer.

3.3 Water barrier property

The water vapor permeability (WVP) coefficients of PLA/BC biocomposites were shown in Fig. 4 and Table 3. Surprisingly, the results showed that incorporating ground BC resulted in the increased water vapor permeability for the PLA/BC biocomposites compared to the neat PLA. As the nature of cellulose is hydrophilic, therefore, water molecule could dissolve in the PLA/BC biocomposites better than the neat PLA. Consequently, the water vapor could transfer through the PLA/BC biocomposite better than the neat PLA. Among the PLA/BC biocomposites, the water vapor permeability coefficients increased with an increase of the BC particle sizes from <90 μm to 180-250 μm.

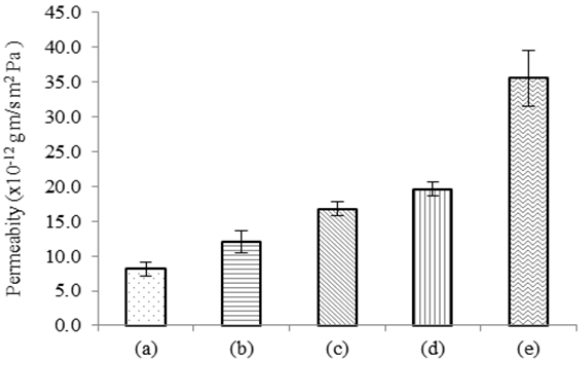

Fig.4. Effect of BC particle sizes on water vapor permeability of the biocomposites: (a) neat PLA; (b) PLA/BC <90; (c) PLA/BC 106-125; (d) PLA/BC 150-180; (e) PLA/BC 180-250 μm.

These results showed disadvantage of the incorporation of ground BC into the PLA matrix, which are not agreed with the incorporation of cellulose nanofiber into the same polymer reported by Fortunati and co-worker [9]. It was observed that cellulose nanofiber not only improved the water vapor barrier, but also modified the biocomposite surface minimizing the water vapor barrier. In the present work, the highest water vapor permeability was obtained with the BC particle size 180-250 μm, an increased 338% compared to the neat PLA. This might be loading the larger BC particle size leads to agglomerate the BC particle, resulting in the roughness surface of PLA/BC biocomposites. This confirmation is clearly visible with SEM micrograph (Fig. 5). Thus, the water vapor permeability was higher when loading the smaller size of BC particle. In contrast, with loading the smaller particle, the cellulose nanocrystal was resulted in decreased water vapor permeability of the PLA nano-biocomposites [9]. As the hydrophilic nature of cellulose, the water absorption in the PLA/BC biocomposites was induced to increase the biodegradability of PLA/BC biocomposites [11].

Table 3.The effect of BC particle sizes on water vapor permeability of the PLA/BC biocomposites.

Samples	Thickness (mm)	Permeability coefficient ($x10^{-12}$ g m/s m^2 Pa)	Increasing (%)
Neat PLA	0.317	8.11±0.99	-
PLA/BC <90 μm	0.350	12.08±1.57	48.9
PLA/BC 106-125 μm	0.438	16.72±1.00	106.2
PLA/BC 150-180 μm	0.426	19.59±1.00	141.6
PLA/BC 180-250μm	0.448	35.52±3.94	338.0

3.4 Morphology

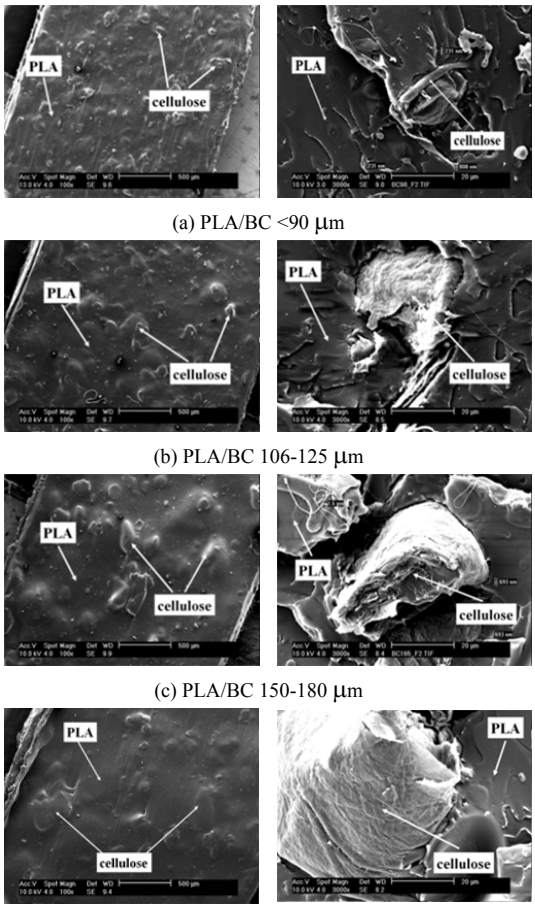

Fig.5. Scanning electron micrographs of surface (left) and freeze fracture surface (right) of the biocomposites.

Scanning electron microscopy images of surface and freeze fractured surfaces of the PLA alone and its biocomposites were shown in Fig. 5. From these scanning electron micrographs, the BC particle sizes clearly affected on the dispersibility of ground BC in the PLA matrix. The smaller BC particle sizes were loaded, the smoother PLA/BC biocomposites were found due to an aggregation of cellulose particles. This implied that the smaller BC sizes could disperse better in PLA matrix than the larger particle sizes did. For example, the comparison between the largest BC particle size (PLA/BC 250-300 μm) and the smallest BC particle size (PLA/BC <90 μm), the former showed the size of agglomerated BC was larger than that of the latter one. Moreover, loading the larger particle size of BC tends to agglomerate and float at sheet surface. This might be leads to form the pin hole on sheet and increasing of water vapor permeability. As expected, an improvement PLA/BC biocomposites harnessing the BC dispersibility could be performed with the surface modification of BC before incorporating into PLA matrix.

4. Conclusion

The mechanical properties of PLA/BC biocomposites decreased with an increase of the BC particle sizes. This was agreeable correlated with morphology, in which the smaller BC sizes could disperse better in PLA matrix than the larger particle sizes did. For the thermal properties, BC lowered the peak crystallisation temperature of the

biocomposite films to 112.2-113 °C from 119.8 °C (the neat PLA film). This behavior indicated that the bacterial cellulose could induce crystal nucleation of the PLA polymers. However, BC did not effect on the T_g or T_m. In contrary, the water vapor permeability of the PLA/BC biocomposites were increased with an increase of the BC particle sizes. The crystallization of the biocomposites will be promisingly improved with the heat-treatment, and those for the biodegradation in soil by burial test and/or the hydrolytic degradation are to be approved.

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